STEM characterization of solar cells

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X.1 Introduction

Photovoltaic (PV) devices consisting of a thin-film CdTe absorber layer on glass support have long been considered one of the leading technologies for reaching the Department of Energy's 2030 cost target of less than $0.03/kWh. The currently used device architectures include a thin transparent conductive oxide (TCO) on top of the glass superstrate following by very thin (<100 nm) polycrystalline emitter layer, typically CdS or more recently MgZnO (MZO)[1]. The CdTe absorber layer is usually up to 4 µm thick and polycrystalline, followed by the back contact (Figure 1). Typical CdTe thin-film layers are formed from rapid deposition techniques, such as close-spaced sublimation (CSS) or high-rate vapor-transport deposition (HRVDT). Both processes result in a polycrystalline CdTe photo-absorbing film [2], and such devices can be manufactured cheaply and efficiently at large scale. Record cell efficiencies as high as 22.1% have been demonstrated [3]. However, such cell performances are still far from the theoretical limits (~30% for CdTe) [4], and improvements have mostly been due to better light collection, rather than improvements in absorber conversion efficiency. The remaining obstacles to further improving these devices toward their theoretical limits concern improvements in the fill factor (FF) and, more importantly, open-circuit voltage (V_{oc}), which is still far from its limit [5]. In fact, it is widely accepted that V_{oc} is the limiting factor since it reaches only about 60% of the CdTe bandgap. This is in contrast to GaAs solar cells, which have reached a V_{oc} of 80% of the bandgap. The reasons for this discrepancy have been identified as the low *p*-type doping concentrations of CdTe due to the formation of compensating defect states, a poor *p-n* junction, and the need for better backside ohmic contacts. High interfacial defect density at grain boundaries (GBs) and intragrain dislocations is also one of the main concerns because they contribute to the dark current [6]. This is supported by the study of single-crystal-based CdTe solar cells that were able to reach V_{oc} in excess of 1 V [7, 8].

Minority-carrier recombination outside of the quasi-neutral region therefore severely limits the V_{oc} and can play a powerful role in determining the FF. The carrier lifetime is primarily limited by defect-mediated, nonradiative, Shockley-Reed-Hall (SRH) processes [9, 10]. Such nonradiative recombination within the CdTe grain-boundary network limits V_{oc} and to a lesser extent the Fill-Factor (FF). Thus, improvements in the FF and V_{oc}—and ultimately, efficiency—can be accomplished through defect mitigation to prevent recombination of carriers as they move through the device. Over the years, many approaches have been developed to mitigate these defects, most notably the $CdCl_2$ treatment, which has numerous beneficial effects [11, 12]. Yet, the work-function mismatch between available materials and the CdTe absorber causes significant forward resistance and a reduction in the conversion efficiency by further reducing the FF.[13] Therefore, a better understanding of the electronic behaviors of defects and of the atomic structure–property relationships are needed.

FIGURE 1 HERE

Due to the structural complexity of the GB network and the bulk defect structures found within the grains, transmission electron microscopy (TEM) has been used extensively to determine the structure-property relationships of CdTe thin-film devices. In 1989, Lu and Smith studied the atomic structure of dislocation cores in CdTe using TEM [14]. The authors found two types of partial dislocations, 30° and 90°, resulting from the dissociation of 60° dislocations, and the dislocations exhibited glide and shuffle sets. Yet, the chemical composition of such partial dislocations could not be analyzed directly until the introduction nearly 25 years later of aberration correctors and large-area X-ray detectors [15, 16].

The structure of twin boundaries, where the stacking sequence of the (111) planes in the twin region is changed with respect to the host lattice, was first characterized by Durose and Russell using TEM [17]. The authors identified two types of twin-boundary structures: a Σ3 (first-order) and Σ9 (second-order) twin lying along different crystallographic planes. Such twin-boundary structures are prevalent in most grains within thin-film CdTe PV devices and have been studied extensively since 1990. The atomic structures have been resolved using aberration-corrected scanning transmission electron microscopy (STEM) imaging [18], and the chemical composition of twin boundaries in as-grown and $CdCl_2$-treated grains was determined using electron energy-loss spectroscopy (EELS) and X-ray energy-dispersive spectroscopy (XEDS) [19]. It is widely accepted that twin boundaries in $CdCl_2$-treated CdTe forming stoichiometric Σ3 interfaces that penetrate the entire grain are electrically inactive as far as electron-hole recombination is concerned. However, Li *et al.* [20] found that when twin boundaries terminate within a grain, a Cl-doped dislocation core at either end of the twin boundary establishes an electro-static potential that helps separate charge carriers which is beneficial for carrier-collection efficiency [20]. Meanwhile, in 2003, Yan *et al.* [21] imaged the atomic structure of edge dislocations in CdTe, finding that the dangling bonds at the dislocation core create midgap states in CdTe, which are responsible for the high SRH recombination rates found in CdTe GBs. The presence of Cl at CdTe grain boundaries after the $CdCl_2$ annealing, as reported by Li *et al.* [20], passivated the dislocation cores and reduced the density of midgap states.

In this chapter, we will summarize some of the more recent results of atomic-resolution transmission electron microscopy of defects and grain boundaries in CdTe. Aberration-corrected STEM has developed into a powerful tool to characterize the local atomic and electronic structures of materials. Due to the incoherent nature of the imaging process, the atomic-resolution high-angle annular dark-field (HAADF) images can be used directly to determine the atomic configurations at GBs or dislocation cores. Moreover, recent developments in spectrometer technology now enable atomic-resolution chemical quantification and measurements of the local density of unoccupied states above the Fermi level. When combined with first-principles modeling, electron-beam induced current measurements, or device-level modeling, STEM characterization can provide powerful information about the role that GBs and individual defect complexes play on V_{oc}, FF, and thus, the overall cell conversion efficiency.

The remainder of this chapter is organized as follows: We will first describe the working principle of analytical STEM, followed by several examples where atomic-resolution STEM imaging was combined with EELS and XEDS to study grain boundaries in CdTe. We will then briefly discuss how STEM imaging can be combined with first-principles modeling to explore new passivants. We conclude by providing an outlook of possible new developments in STEM approaches for CdTe devices that can potentially address the outstanding issues limiting the performance of polycrystalline CdTe thin-films devices.

X.2. Scanning Transmission Electron Microscopy

Imaging and chemical analysis in an aberration-corrected STEM has become one of the preeminent tools for studying the local atomic and electronic structure of materials. The state-of-the-art aberration-corrected STEM allows for atomic-resolution incoherent imaging using HAADF imaging [22]; but it can also be used to perform high spatial-resolution microanalysis using EELS and XEDS [23]. The atomic-resolution HAADF detector, which forms images by registering electrons that have scattered to high angles, provides contrast where the image intensity depends directly on the atomic number of the imaged atomic columns.

While aberration correction has made crucial contributions toward improving the spatial resolution and beam current in conventional STEM setups, the integration of cold field-emission gun (CFEG) electron sources now allows for sub-angstrom (sub-Å) spatial resolution with sub-eV energy resolution to determine the atomic structure as well as atomic-level chemical composition and local bonding. When HAADF imaging is coupled with simultaneous XEDS or EELS acquisitions, the atomic structures of the crystal lattice can be resolved directly (if the sample is orientated along a zone axis) and the chemical composition and local bonding can be measured at similar spatial resolutions. This makes STEM an indispensable tool for identifying defect structures in CdTe, GaAs, and other thin-film materials.

Figure 2 shows a schematic drawing of the STEM optical configuration. A series of magnetic lenses is required to provide the desired demagnification of the CFEG electrons onto the sample surface to form an atomic-scale electron probe. The condenser lenses (CL) provide initial demagnification for the objective lens (OL), which provides the final and largest demagnification. Aberrations introduced by this strongest focusing lens dominate the optical system, which can only be corrected by using a series of multipoles lenses that provide negative spherical aberrations to compensate positive spherical aberrations introduced by objective lens.

FIGURE 2 HERE

The aberration-corrected electron probe is scanned across the surface of the sample using a set of scan coils. Electrons scattered by the specimen in the forward direction are detected by scintillator detectors in the far-field diffraction plane and plotted as functions of probe position to form STEM images. STEM imaging modes are defined based on which angular ranges are used for signal integration within annular detectors centered on the optic axis. These are typically distinguished whether the bright-field (BF) or dark-field regions (DF) are used. The former is defined by the convergence semi-angle of the electron probe and for atomic-resolution imaging is typically 15-30 mrad or more. Signal in the BF region exhibits pronounced interference between elastically scattered and the unscattered electrons. However, placing an annular detector in the outer half of the BF disk results in the so-called annular bright-field (ABF) imaging mode that still shows little-to –none image contrast reversal in typical imaging conditions [24, 25]. ABF is widely used for atomic-resolution imaging of crystals that may contain light element atomic-columns, such as oxygen, lithium or even hydrogen [26-28]. HAADF is by far the most popular imaging mode within the DF region that utilizes quasi-elastically and thermally scattered electrons [22, 29-34]. The image contrast in HAADF scales directly with atomic number of the atomic-column species ($\sim Z^{1.8}$) and so images can be directly interpreted in terms of the lattice structure. Low-angle DF region (LAADF) shows some coherence effects and can be also useful since LAADF enhances contrast from locally strained lattice. The above mentioned images can be acquired simultaneously within a STEM instrument equipped with several annular detectors.

STEM image simulations can be used to refine an atomic lattice structure or to interpret images within highly strained regions, such as dislocation cores. Two main approaches exist to simulate dynamical electron propagation in STEM: 1) The Bloch wave method is based on solving the three-dimensional time-independent Schrödinger equation within the crystal structure. The electron wavefunctions at the exit surface of the specimen are calculated after solving the eigenvalues and eigenvectors of the scattering matrix with appropriate boundary conditions. The Bloch wave method provides an intuitive picture of electrons propagating within the crystal in terms of Bloch waves. However, in complicated structures with defects and interfaces, the huge number of Bloch waves makes a Bloch wave matrix solution impractical [35]; 2) The multislice method divides the specimen into thin two-dimensional slices along the incident-beam direction and implements wavefunction propagation within the crystal. The defect structures and 3-D crystal shape can easily be accounted for in this method [36, 37].

Whereas the high-angle quasi-elastic scattering is used for HAADF images, the small-angle inelastically scattered electrons can be coupled into an electron energy-loss to form an EEL spectrum. The inelastically scattered electrons are separated according to their kinetic energy by a magnetic prism, and the signal intensity is plotted as a function of energy channels. EEL spectrum contains three major parts: the 1) zero-loss peak, 2) low-loss , and 3) core-loss parts. The zero-loss peak contains spectroscopic information about the energy resolution of the electron microscopy system, but also acts as the zero-energy reference point for the rest of the spectrum. The specimen thickness information in terms of inelastic-scattering mean free path can also be extracted from the low-loss regime [23]. Low-loss spectra are characteristic of the outer-shell electron excitations, including the optical properties of the specimen, reflecting the dielectric information of the material. Core-loss spectra reflect the density of unoccupied states above the Fermi level, and the near-edge fine-structure contains valuable information about the local bonding and long-range order. EELS excels at the chemical analysis of light elements such as C, N, O, or Cl, which have well-behaved core-loss edges within the 1.5-keV range. In characterizing CdTe solar cells, EELS is used to show Cl segregation along GBs and other interfaces.

Energy-dispersive X-ray spectroscopy is another approach to characterize the chemical composition of materials in STEM. In XEDS, heavy and light elements can be analyzed easily making of use characteristic X-rays that are generated when an electron transitions from an excited state to the ground state. The characteristic X-ray peaks are little affected by the chemical environment, which makes XEDS highly reliable in quantifying chemical composition of a specimen. The development of aberration correctors and cold field emission (CFE) sources makes it possible to acquire atomic-resolution XEDS in STEM. The modern silicon drift detector (SDD), such as the Oxford XMAX 100TLS, considerably increases the X-ray-collection solid angle, which improves the counts rate and acquisition speed. Atomic-resolution XEDS mapping enables one to identify chemical composition within defect cores appearing in CdTe solar cell thin films [38].

Specimen preparation is essential for successful atomic-resolution STEM characterization of materials. To achieve atomic-resolution STEM imaging, the specimen must be electron transparent and representative of the material. For STEM characterization of CdTe thin film, focused ion beam (FIB) is a commonly used technique to make cross-sectional TEM specimen. The constant thickness of the lamella makes FIB an ideal technique for quantitative analysis of chemical composition. For the dual-beam system with a scanning electron microscope (SEM), precise areas can easily be selected under secondary-electron imaging. However, high-voltage ion bombardment may cause artificial structure change and gallium ion implantation. Particularly for CdTe-based specimens, low-voltage gallium or argon ionic cleaning is necessary. There are some indicatios that the Cl concentration within CdTe thin films might be affected by the FIB process. In this case, conventional polishing with Ar milling at liquid nitrogen might be needed.

X.3. Structural and Chemical Characterization of CdTe Solar Cell Devices

Polycrystalline CdTe-based solar cells have undergone improvements and optimization in their growth conditions and post-processing steps over the years to reach the present-day cell efficiencies of more than 22%. High-resolution transmission electron microscopy has played a pivotal role in this process by providing insights into the device morphology and chemical composition, thus helping to optimize synthesis methods. Here, we highlight how aberration-corrected STEM characterization approaches have been applied to CdTe solar cells, resulting in advances in today's fundamental understanding of this technology. This sets the stage for the atomic-resolution analysis of defect structures, as well as the need for correlative experimental and first-principles computational methods that assume increasing importance in developing CdTe-based photovoltaics.

A cross-sectional image of a polycrystalline CdTe solar cell is shown in Figure 1. The image was acquired with aberration-corrected STEM using ABF mode by integrating electrons scattered within a cone from 11 to 22 mrad with respect to the optic axis [25]. This imaging mode can provide contrast superior in some cases to HAADF or conventional bright-field TEM, especially for polycrystalline features and material compositions at lower magnifications, as well as at atomic resolution of low atomic-number (Z)-containing materials [39, 40]. Here, a typical CdTe solar cell grown in a superstrate configuration after a post-deposition $CdCl_2$ heat treatment is shown with marked layers: transparent conductive oxide (TCO) composed of fluorine-doped tin oxide ($F:SnO_2$), CdS emitter/window, and *p*-type CdTe absorber layer, the latter forming the heterojunction. Numerous micrometer-sized CdTe grains are visible, with smaller grains often found near the interface with CdS. Low interfacial energy of stacking faults in CdTe and typical growth conditions favor formation of numerous twin boundaries within the interior of randomly oriented grains. These can be clearly seen in Figure 1 as brighter and darker stripes extending through an entire grain.

The performance of the CdS-CdTe heterojunction is crucial to high cell conversion efficiencies. The CdS layer is preferably kept as thin as possible, typically 30–50 nm, to reduce its absorption in the blue portion of the visible spectrum, which can otherwise reduce the short-circuit current. However, studies showed that CdS synthesized via phase-vapor deposition (PVD) in the absence of oxygen undergoes large interdiffusion with CdTe in the subsequent growth and high-temperature $CdCl_2$ processing [6, 41-44]. This leads to the formation of CdS_yTe_{1-y} alloy nanocrystals with reduced optical bandgap and possibly produces graded-like lattice matching of CdS and CdTe. However, in some cases, this interdiffusion can consume parts of CdS entirely, creating local shunting pathways. Introducing O_2 into the PVD environment, as well as its presence in CSS and other sputtering deposition approaches, has been credited with suppressing such interdiffusion. Furthermore, it has been suggested that CdS with higher oxygen content exhibits higher bandgap, which would be beneficial to reduce the aforementioned absorption [41].

It is crucial to be able to map the distribution of light elements with nanometer spatial resolution to elucidate how the mixing occurs. Such characterization has been performed using STEM in combination with either with EELS or XEDS [23, 45]. EELS generally provides a better signal-to-noise signal ratio over XEDS because most of the inelastically scattered electrons are collected for analysis. However, this depends on whether the element of interest has a strong core-electron ionization fingerprint. Furthermore, present-day dual-EELS systems allow the selection of two rather narrow energy windows for acquisition; so, a completel elemental sample mapping can rarely be performed. The introduction of large solid-angle, windowless, silicon drift detectors (SSDs) in recent years now allows increased sensitivity to X-rays from lighter elements. In addition, semi-automated quantification based on *k*-factors and ability to simultaneously map emissions from all elements present in a sample has made XEDS a highly attractive technique [16, 45].

An illustration of CdTe solar cell large-area XEDS elemental mapping is shown in Figure 3. In this study, the authors examined the role of oxygen on the properties of the *p*-*n* junction [41]. CdS layer thickness and its composition can be seen to vary considerably. Although oxygen appears to be retained in some parts of CdS, other parts show oxygen-rich clusters in a form of $CdSO_x$ phase. Intermixing of CdS-CdTe at the interface as well as small parts of nearly consumed CdS layers can be seen in the images and extracted line profiles shown in Figures 3(b) and 3(c).

FIGURE 3 HERE

The post-deposition annealing of CdTe solar cells in $CdCl_2$ is another standard post-processing step that is crucial for high performance of the solar cells. Several changes occur during this so-called activation of CdTe cells, which are reflected in all the key PV parameters, bringing the conversion efficiency up by as much as 10 percentage points [6, 41]. First, CdTe recrystallizes, leading to coalescence and the growth of grains to diameters of 1–2 micrometers. This morphological rearrangement likely reduces the number of interfacial defects associated with GBs and bulk defects that are detrimental to device performance. Furthermore, Cl is found to diffuse strongly throughout CdTe and is expected to occur much faster along GBs than in the bulk [46]. Enrichment of the CdS-CdTe interface with Cl as well as of CdTe GBs is widely reported in the literature [6, 19]. This can also be seen in the XEDS elemental maps shown in Figure 3. Combined electron-beam induced current (EBIC) and STEM-density functional theory (DFT) studies suggested that Cl helps to passivate dangling bonds associated with interfacial and bulk defects [18, 47-49]. This is reflected in enhanced carrier-collection efficiency and reduced interfacial recombination.

Support for this view also comes from atomistic simulations of defect structures in CdTe. Segregation of Cl at grain boundaries in CdTe is often found to correlate with reduction of Te at these interfaces. Figure 4 shows GB EELS chemical mapping at an intersection of three randomly oriented grains [49]. Enrichment of Cl is apparent and is coupled with reduced Te signal with no significant change in Cd concentration. This type of Cl-Te substitution was reported to be energetically favorable for the studied dislocation cores. The authors found that the exchange can lead to removal of midgap states introduced by defects, which, in turn, reduces recombination centers that impact charge-carrier lifetimes [50, 51]. Another benefit of GB enrichment with Cl is suggested to arise if local *p*-*n*-*p* junctions are established across these interfaces [20, 52]. The local electric field would promote carrier separation and enhance their collection efficiency.

FIGURE 4 HERE

Post-deposition $CdCl_2$ annealing of CdTe solar cells is typically followed by Cu diffusion treatment [53, 54]. Although the interplay between these treatments is still an active research topic, Cu is thought to serve in several ways. As-grown CdTe is slightly *p*-type due to Cd vacancies and is hole-doped with diffused Cu to the typically reported levels on the order of 10^{15} at/cm^3 [6, 55, 56]. No significant segregation of Cu at grain boundaries in CdTe and the *p-n* junction has been reported in the literature. However, such Cu segregation would be a concern because it could lead to detrimental effects by compensating the emitter or creating shunts. Another important role played by Cu is formation of the back contact. A more heavily doped *p*-type surface layer combined with Te alloying is usually employed to promote formation of ohmic contacts.

In the next section, we will show how advanced atomic-resolution STEM studies can be used to characterize the defect structures in CdTe. These studies have paved the way to fundamental understanding of atomic-scale effects, and combined with atomistic simulations, they have provided new insights on how to advance CdTe photovoltaic technology.

X.4. High-Resolution Imaging and Spectroscopy

Recent developments in aberration-corrected STEM instrumentation have allowed for investigations of defect structures with sub-Ångstrom spatial resolution. Incoherent HAADF imaging mode is typically employed, which provides images where the contrast can be directly correlated to the sample thickness and the atomic number (Z) of the constituent atomic columns [39]. Readily available and fast quantum-mechanical image simulations can be further employed to refine the structure and identify, e.g., positions of light or heavy dopant atoms [37, 57]. Sample imaging can be coupled with simultaneous acquisition of XEDS or EELS signals to obtain information about the chemical composition of the atomic columns. This has led to rapid cataloguing of a plethora of different types of dislocations and their atomic-core structures that naturally form within polycrystalline CdTe films [15, 18, 20, 52, 58].

Figure 5 shows several atomic-resolution HAADF images of CdTe along its <110> crystallographic direction [49]. In this projection, CdTe appears as a collection of closely spaced atomic columns (dumbbells) that are each natively composed of either Cd or Te atoms. Due to the difference in the atomic number of Cd and Te ($Z_{Cd} = 48$, $Z_{Te} = 52$), inspection of the HAADF image contrast allows one to determine their polarity in the bulk. However, atomic-column-resolved XEDS or EELS is still preferred for unusual dislocation-core configurations that may also contain point defects or be strained, where the contrast in HAADF images is less reliable in gauging chemical composition. Although atomic-resolution information can be obtained along several CdTe zone axes, such as <112>, mixed-column <111>, and others, the <110>-type zone axis is by far the most preferred. Burgers vector of an elemental glide-set dislocation system (111)<110> in zinc-blende materials makes a 60° angle with respect to the dislocation line, thus having both edge and screw components. Dislocation lines are oriented parallel to the <110> direction, so that their core structures as well as their Burgers vector edge-component can be determined by imaging along this zone axis. Although there is ambiguity regarding the screw component, knowledge of the edge part is often sufficient for determining the type of dislocation in an HAADF image [15].

FIGURE 5 HERE

Due to small interfacial stacking fault energy, dislocations in bulk are usually found dissociated into a pair of Shockley partial dislocations joined by an intrinsic or extrinsic stacking fault. Two such dissociated dislocations are shown in Figures 5(a) and 5(b), respectively. The Burgers circuits drawn around the dislocations show enclosures, or lack thereof, and define the edge component of the dislocation. Similar circuits can be drawn around each partial dislocation core crossing through the stacking fault. For example, it was found that the two partials in Figure 5(a) are both 30° Shockley partial dislocations but with opposite edge components, concluding that this is a dissociated screw dislocation. The cores are terminated with single atomic columns that are Cd and Te, respectively. These core configurations indicate an atomic under-coordination with respect to the natural tetrahedral bonding in CdTe, suggesting the presence of dangling bonds. Similar analysis can be performed for the dissociated elemental dislocation in Figure 5(b). More complex interacting dislocations were also reported in CdTe crystals. Figure 5(c) shows an atomic-column-resolved XEDS image of a Lomer-Cottrell dislocation junction-core overlaid on top of the HAADF image [15]. This type of dislocation junction can be formed by the intersection of two 30° Shockley partial dislocations from different sets of (111) planes making the acute angle, or a dislocation cross-slip onto another (111) plane. The dislocation core is seen to be Cd_3Te-type. Due to the crystallographic polarity of CdTe, a $CdTe_3$ variant of Lomer-Cottrell junction also exists and was reported in the literature. First-principles DFT calculations show electrical activity on 30° and 90° dislocation cores as well as the structural unit Cd_3Te, and it will be discussed in more detail in the following sections [18, 20, 52, 59].

Before we go on to discuss atomic-resolution characterization of general CdTe grain boundaries, we briefly come back to twin boundaries seen in Figure 1. Stacking faults and lamellar coincidence-site lattice (CSL) Σ3 (111) twin boundaries are the simplest and most abundant interfacial defects in CdTe. Atomic-column-resolved XEDS maps of a typical stacking fault on a (111) plane are shown in Figure 5(d) [16]. Unlike the defects discussed above, this interface has no dangling bonds and its atoms satisfy the tetrahedral coordination. Computational studies suggest that this configuration is indeed electrically benign. Interaction of twin boundaries with native point defects was also reported in the literature using combined STEM and DFT approaches [19].

Five macroscopic degrees of freedom are required to define a most general GB, in addition to microscopic ones related to atomic relaxations. Electron back-scattering diffraction (EBSD) analysis of grain distributions in polycrystalline CdTe indicates no special preference for their orientations [60]. This excludes the above-mentioned intragrain lamellar twins, which may be viewed as a GB formed by a 180° twist around the interface normal <111>. Although the grains in CdTe are randomly oriented, a great majority of them reported in the literature nevertheless share the tendency for Cl segregation and the accompanying Te depletion along their boundaries. This provides motivation to investigate GB structures—or, more generally, CdTe interfaces—in more detail to find the underlying reasons for this tendency and possibly shed new light on how to introduce more potent passivating agents. Due to random GB orientations, the practical limitation in this approach is locating two or more grains sharing boundaries that can be simultaneously imaged at atomic resolution to reveal the interface structure. There are only a handful of crystallographic zone axes suitable for STEM imaging, at least with present-day instrumentation, and this limits the types of GBs that are possible to observe.

Various tilt, as well as CSL, grain boundaries were studied in polycrystalline CdTe [15, 19, 20, 58]. A tilt GB imaged along <110> is shown in HAADF Figure 6(a). Here, the interface is found to be composed of repeating structural units of the Te_3Cd-type, similar to the one shown in Figure 5(c). Chlorine segregation and Te depletion is observed to occur in this interface as well, as seen in EELS line profiles in Figures 6(b) and 6(c). A HAADF image in Figure 6(d) shows the same structural units in the CSL Σ3 (112) grain boundary with dense twinning. The high-resolution XEDS mapping in Figure 6(e) indicates a localized Cl segregation within the structural units and Te depletion. Thus, it appears that certain atomic structural units may be more prevalent in CdTe.

FIGURE 6 HERE

Another approach, as opposed to the heuristic scan of polycrystalline CdTe samples for suitably oriented grains, is to produce artificial GBs with already pre-determined crystallographic orientations. This entails bonding single-crystal CdTe wafers with chosen interfacial planes, twist, and tilt angles such that the zone axes of the crystallites allow for reliable atomic-resolution STEM characterization. An added benefit of this approach is that auxiliary electro-optical measurements can be performed and that processing steps can be tested on such structures, e.g., $CdCl_2$ treatment, or of other passivating agents. One concern of this approach is how reliably these structures represent GBs that naturally occur within polycrystalline CdTe. Some very high interfacial-energy interfaces would likely have to be ruled out. However, this could still allow for a non-trivial part of the GB configuration to be investigated.

In the following, we look at a correlative STEM-DFT study of a low-angle tilt artificial GB created by wafer bonding [61, 62]. Two single-crystal CdTe wafers with (110) surfaces and a 2.4° symmetrical off-cut were used, as shown in Figure 7, producing a 4.8°-tilt GB. Tilt GBs in simple cubic materials are predicted to be composed of discrete edge dislocations along their interface, with the spacing increasing toward small tilt angles. However, it is not easy to predict what resulting dislocations and their arrangements—or some other structural units altogether—are going to be found for any given interfacial boundary plane [63]. In the GBs studied here, dislocations were mostly pure-edge Lomer dislocations, which can be seen as resulting from two merged 60° elemental dislocations with opposite screw components. Individual elemental 60° dislocations and dissociated variants were also found to a lesser extent. This could be due to compensating dislocations with opposite screw components present in the vicinity or an unaccounted small twist of the crystallites. Atomic-resolution HAADF imaging of the dominant dislocation core is shown in Figure 8. It is seen to be composed of 5–7 and 6–8 atomic rings. A seed structure based on the HAADF image was used for DFT structural relaxations. The relaxed model is shown overlaid on the experimental image, giving a nearly perfect match. The electronic structure analysis of these defect cores and the behavior of such a GB are discussed below.

FIGURE 7 HERE

Two other examples of wafer-bonded GBs are shown in Figure 9. A 8°-tilt GB with (111) interface plane is seen in Figure 9(a). An extra (111) plane emerges at each dislocation core every ~5 nm. This GB is composed solely of 60° elemental dislocations that carry large screw components. A possible explanation is that the dislocations' screw components alternate between parallel and anti-parallel orientations along the interface to accommodate the pure tilt. An inset shows a geometrical phase-analysis (GPA) strain-field mapping of the interface [64, 65]. In particular, local lattice compression (green) and tension (red) in the horizontal image direction (e_{xx}) is mapped, generating dipole-like strain fields by the edge components. The strain fields of adjacent dislocations overlap negligibly so that the interface electronic properties could still be approximated by considering individual defects.

FIGURE 8 HERE

A more exotic GB formed by wafer bonding is shown in Figure 9(b). Polar Te-terminated (001) crystal surfaces for both crystallites were chosen here as the interface plane, thus defining a 180°-tilt GB. An atomic-column-resolved XEDS map overlaid on the simultaneously acquired HAADF image shows chemical composition of the interface marked with a dashed yellow line. The interface is Te-rich and demonstrates long-range order. A closer look also reveals formation of triple-column structures on the left-hand side of the interface.

FIGURE 9 HERE

X.5. Correlating STEM Imaging with DFT Modeling

Atomic-resolution imaging and EELS as well as XEDS spectroscopies can be used to determine the local composition and crystal structure. But first-principles modeling is needed to correlate the observed feature with the local density of states (DOS), the transport properties, and carrier lifetime properties. Here, we will show how a combination of STEM imaging and DFT modeling can be used to investigate the roles of dislocation cores and GBs in CdTe polycrystalline thin-film devices.

First, the HAADF images are used to determine the dislocation core structure by extracting the atomic-column locations directly from the atomic-resolution images. These two-dimensional projections are then extended in the third dimension, and the positions of the atomic columns are refined using first-principles DFT modeling, as shown in Figures 10(c) and 10(d). Next, the DOS and local charge density are calculated using Bader charge analysis for edge dislocations as well as Σ3 (111) (or twin) GBs. It was found that dislocation cores show significant charge transfer compared to bulk CdTe. This charge transfer results from the changes in coordination at the dislocation core center, which can introduce additional states in the bandgap. This result for the dislocation is in contrast to the Σ3 (111) GBs, which exhibit features very similar to that of bulk CdTe.

FIGURE 10 HERE

The electronic structures, or DOS, calculated for the dislocations core structures shown in Figure 10, as well as the Σ3 (111) twin boundary, are shown in Figure 11. Figures 11(c) and 11(d) clearly show that the dislocation cores give rise to additional states within bulk bandgap. Those extra midgap states act as SRH recombination centers, which will lower the minority-carrier lifetime considerably, and thus, they affect the overall efficiency of the CdTe solar cell. Σ3 (111) twin boundaries do not exhibit any midgap states compared to bulk CdTe because there are no dangling bonds found at the twin boundaries. This finding is in good agreement with the experimental results that found Σ3 (111) twin GBs to be electrically inactive and having no effect on the electron-hole recombination rates.

FIGURE 11 HERE

Next, we will show how the effects of Cl segregation along GBs in polycrystalline CdTe thin films can be addressed using DFT calculations. Figure 12(a) shows the relaxed structure of an edge dislocation, where Te atomic columns have been replaced by Cl. The DOS of such Cl-passivated dislocation cores is shown in Figure 12(b). It can clearly be seen that the Cl-passivated dislocation cores exhibit a substantial reduction in midgap states compared to pristine cores. This effect has been attributed to the presence/passivation of Cl at the dislocation core center, and it results in significantly reducing recombination sites and increasing minority-carrier lifetimes in CdTe thin films that have been treated with a $CdCl_2$ annealing step. Therefore, the correlation of experimental STEM with theoretical DFT calculations explains the role of dislocation as recombination centers in CdTe thin films and demonstrates the important role of Cl segregation in passivating midgap states as well as improving CdTe solar cell efficiency.

FIGURE 12 HERE

In addition to the GB passivation effect, Cl segregation was also considered to form a local *p-n-p* structure along GBs. Using aberration-corrected HAADF imaging and electron spectroscopy, Li *et al.* studied the atomic structure of Σ9 GBs in CdTe thin films. The structure of the dislocation cores is shown in Figure 13(a). First-principles DFT calculations were deployed to determine the electronic structures of the Σ9 GB dislocation cores with Cl passivation as shown in Figure 13(b). These electron-structure calculations show that at sufficient Cl concentrations, the GB inverts from *p*-type to *n*-type. A local *p-n* junction is created by the *n*-type GB and *p*-type grain interior. The thus-formed built-in field now attracts electrons toward the GB and repels holes, which enhances the carrier separation. Figure 13(c) shows the proposed band diagram of a *p-n-p* junction at the grain boundary. This Cl-induced band bending at the GBs can also contribute to the observed improved conversion efficiency of polycrystalline CdTe-based solar cell after the $CdCl_2$ annealing step.

FIGURE 13 HERE

In addition to GBs, stacking faults and partial dislocation cores were also characterized using the combination of aberration-corrected HAADF imaging and first-principles DFT calculations. Stacking-fault structures, which terminate at two partial dislocations within a grain, were identified and their DOS was determined. It was found that the charge transfer caused by partial dislocation cores introduces significant band bending, which encourages the separation of carriers. The authors suggested that an increased density of intragrain stacking faults and partial dislocation cores may further improve the performance of CdTe solar cells [52].

X.6. Conclusions and Outlook

We have shown how atomic-resolution imaging, electron energy-loss spectroscopy, energy-dispersive X-ray spectroscopy, and density functional theory can be combined to determine the fundamental structure-property relationships of defects and grain boundaries in polycrystalline CdTe thin-film solar cell devices. Although these approaches have been used successfully to explain the effects of Cl passivation, numerous questions related to device performance still remain unanswered, including the role of heterointerfaces on carrier lifetimes and the role of grain-boundary potential on carrier separation and carrier mobility.

STEM imaging has developed into a critical tool for atomic-resolution structural characterization. However, an "information gap" still exists between the atomic-level resolution that can be achieved with these imaging approaches and the approaches used to measure electrical activity of a device, such as electron-beam induced current measurements. EBIC measurements are often performed in an SEM with nanometer resolution at best [66]. Poplawski *et al.* acquired cross-sectional EBIC maps of polycrystalline CdTe devices combined with secondary-electron SEM imaging and reported that grain boundaries and twinning defects appear bright whereas the bulk of grains appears dark [43].

Future developments of EBIC measurement capabilities are therefore needed to fill this information gap by developing a novel experimental approach to measure the local EBIC signal during atomic-resolution HAADF image acquisitions. This will require that cross-sectional TEM samples be prepared using conventional FIB lamellas, where the sample is connected to the current read-outs using e-beam-deposited Pt, without limiting the sample stability to perform atomic-resolution STEM imaging, electron spectroscopy (i.e., EELS or XEDS), and potentially EBIC analysis of single-junction CdTe thin-film devices.

Another exciting development recently is 4D STEM [67] and differential-phase contrast imaging (DPC) [68]. These STEM imaging methods acquire a convergent-beam diffraction pattern at each electron-probe position and will enable us to determine the GB potential and local electric field. If used in polycrystalline CdTe thin-film devices, the quantification of the role of Cl or other elements, such as Se, As, or Cu segregation, on the interfacial potential as a function of treatment parameters could be possible. Such additional analytical capabilities will certainly enable the acquisition of more complete datasets that will facilitate device modeling and the discovery of novel dopants, passivants, or device architectures—thus allowing polycrystalline CdTe thin-film devices to finally approach the Shockley-Queisser limit.

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